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TITLE: Optical and Electrical Properties of Amorphous [GeS₂] sub 100-x
Ga sub x Thin Films

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TITLE: International Workshop on Amorphous and Nanostructured
Chalcogenides 1st, Fundamentals and Applications held in Bucharest,
Romania, 25-28 Jun 2001. Part 1

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OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS (GeS₂)_{100-x}Ga_x THIN FILMS

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Results from the study of basic optical and electrical parameters of semiconducting (GeS₂)_{100-x}Ga_x (x=0, 4, 8, 12 at.%) amorphous layers have been summarized. The investigation of the optical absorption has shown that the introduction of Ga leads to a shift in the absorption edge towards lower energies in comparison with GeS₂. The spectral distribution of the refractive index n , accounting the influence of photoexposure, has been specified. The optical energy gap E_g^{opt} has been determined from the Tauc plot $\alpha h\nu = B(E_g^{opt} - h\nu)^2$. The electrical energy gap E_g^{el} has been obtained from the thermal dependence of the conductivity. Both the values of E_g decrease with increasing Ga content. From the current-voltage characteristics, the effective electron mass m in the conduction band, the electron work function χ at the Al/Ge-S-Ga interface and the relative dielectric permittivity ϵ have been determined. The experimental data are in agreement with Christov's theory for injected electron currents into dielectric or semiconducting materials. The observed regularities are related to some structural peculiarities in the Ge-S-Ga system studied.

(Received June 6, 2001; accepted June 11, 2001)

Keywords: Chalcogenide glasses, Amorphous thin films, Photoinduced changes

1. Introduction

Amorphous chalcogenide semiconductors possess a lot of interesting phenomena, which reveal possibilities for using them in microelectronics and optoelectronics - as ovonic threshold and memory switching devices, inorganic photoresists, optical memory disks, etc. The increased interest in them has been connected mainly with their unique peculiarity to record information by irreversible or reversible structural transformations between a disordered and a more ordered state. Exposure to band gap light causes photoinduced changes, which have been studied in detail by K. Tanaka [1,2]. Especially, amorphous Ge-S thin films exhibit remarkable irreversible photo- and thermo-bleaching effects, caused by illumination and annealing, respectively [2,3].

Recently, Ge-S-Ga glasses have been intensively investigated as host materials for fiber-optic amplifiers and infrared lasers by doping with rare-earth elements [4-6]. They have good chemical durability, low phonon energy, high refractive indexes and good glass-forming ability. Besides, reversible and/or irreversible photoinduced effects have been observed in them, which are more pronounced than those in the binary Ge-S system [7,9].

The glass-forming boundaries and basic physicochemical parameters of the ternary Ge-S-Ga system have been determined earlier [10]. The largest photoinduced changes in the optical and physicochemical properties have been found for amorphous (GeS₂)_{100-x}Ga_x thin films [7,8]. The aim of this paper is to summarize the data on basic optical and electrical properties exactly for such compositions (x = 4, 8, 12 at.% Ga), which are important both from fundamental and practical point of view.

2. Experimental

Bulk Ge-S-Ga glasses were synthesized by melting the initial elements (purity of 5N) inside evacuated and sealed quartz ampoules in a rocking furnace. The suitable temperature regime was

determined depending on the composition [10]. The enriched in sulphur samples were heated to $\sim 780^\circ\text{C}$, held at that temperature for 7-8 h and then quenched in ice-water (Ge-enriched compositions were heated to $\sim 1000^\circ\text{C}$). The homogeneity of the glasses was confirmed by optical and electron microscopy. Amorphous thin films were prepared by thermal evaporation (vacuum $\sim 2 \cdot 10^{-5}$ Pa) onto glass substrates. The special design of the evaporator prevented eventual fractional decomposition [11]. The structure of the films was investigated by electron diffraction and the thickness was measured with an interference microscope. The composition was determined by Auger electron spectroscopy and the data showed that it is identical with that of the bulk glasses, with an accuracy ~ 1 at%, according to the used method (Fig. 1).

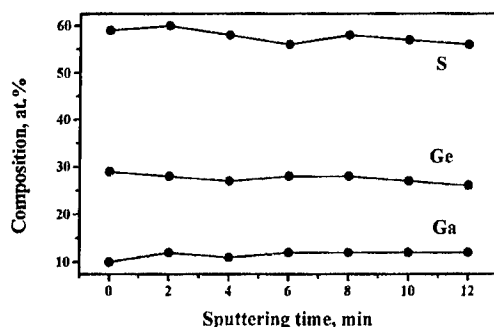


Fig. 1. Profilogram of the Ge₃₅S₅₃Ga₁₂ composition.

The optical transmission was measured in the spectral range of $400 \div 1300$ nm and the refractive index was obtained using a computer program based on a method described by R. Swanepoel [12]. The electrodes were made of extremely pure aluminium (5N) by vacuum deposition. The capacitance and dielectric losses were measured at room temperature with a precise RCL bridge at a frequency of 8 kHz. In order to assess the response of the films to band gap light, half of each film was exposed in air at ambient pressure and temperature by mercury lamp HBO-500 with intensity of about 0.6 Wcm^{-2} .

3. Results and discussion

3.1. Optical properties

It has been found from the investigation of the optical transmittance of amorphous Ge-S-Ga thin films that exposure to band gap light causes a photobleaching effect [8]. The absorption edge shift $\Delta\lambda$ towards shorter wavelengths is accompanied by substantial increase of the integrated transparency of the exposed films. It has been established that $\Delta\lambda$ is maximal for compositions with a ratio of S/Ge=2 and about 10 at% Ga (Fig. 2).

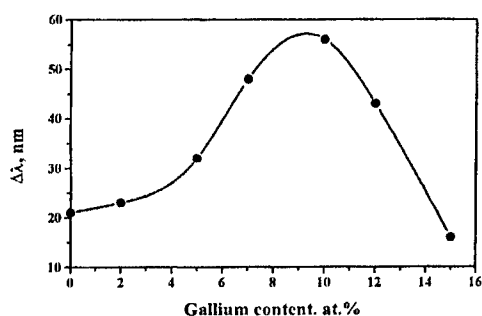


Fig. 2. Compositional dependence of the absorption edge shift.

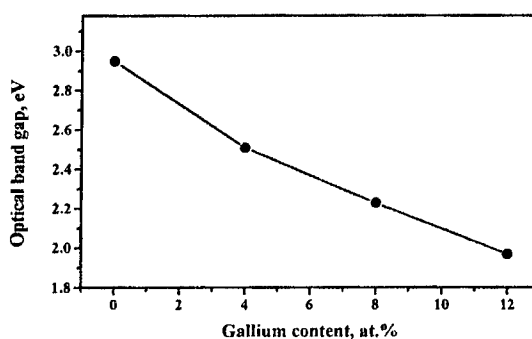


Fig. 3. Compositional dependence of the optical band gap.

The optical energy gap E_g^{opt} has been determined by extrapolating the dependence $(\alpha h\nu)^{1/2} = f(h\nu)$ to the intersection with the abscissa. The E_g^{opt} values decrease from 2.95 eV to 1.97 eV with increasing Ga

concentration, following an weak exponential relation after results fitting (Fig. 3). The refractive index n changes in the same way and its spectral distribution has shown that after illumination n decreases (Fig. 4). The difference Δn between non-illuminated and illuminated films is largest for the composition with 8 at% Ga, which is in accordance with the maximal shift $\Delta\lambda$ (Fig. 2).

It has been found from the Raman spectroscopic study of these films that the photobleaching effect is associated with a certain degree of ordering in the local structure without formation of new phases [13]. This is expressed by enhanced orientation of existing bonds and/or extension of the short range order. Introduction of Ga in the binary Ge-S system results in stronger bleaching, i.e. larger shift of the optical absorption edge to shorter wavelengths. The formed Ge-Ga and/or Ga-Ga bonds are weaker, therefore exposure breaks them to form the basic Ge-S bonds and to bring about a stabilization of the structure. Unfortunately, the Ge- and Ga-containing bonds cannot be distinguished because of their close vibration frequencies and overlapping of the bands.

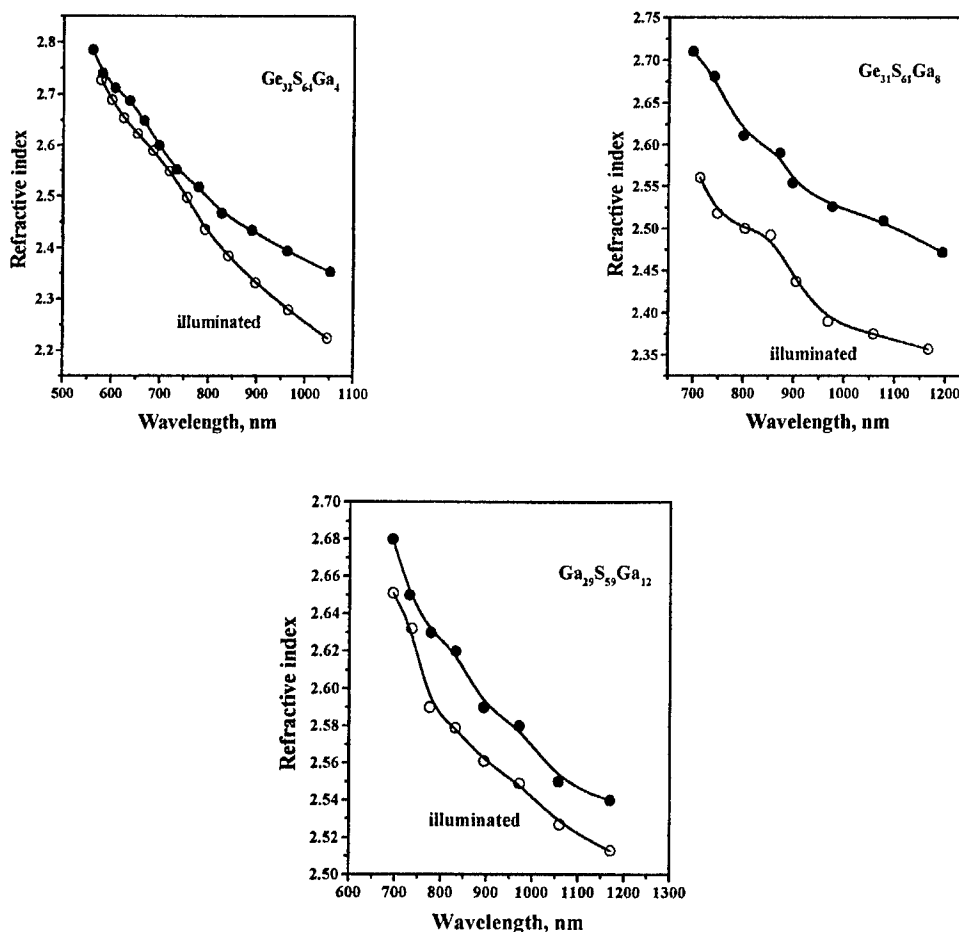


Fig. 4. Spectral distribution of the refractive index.

3.2. Electrical properties

From the current-voltage characteristics, the effective electron mass m^* and electron work function χ at the Al/Ge-S-Ga interface have been determined (Table 1) [14]. An increase of the m^* values at higher gallium content has been observed. The values of the dielectric losses and relative dielectric permittivity are $\tan \delta < 0.03$ and $\epsilon = 6.2 \pm 0.1$, respectively. According to Christov's theory [15], thermionic (T) and thermionic-field (TF) emission regions have been investigated. On the boundary between them, determined by the condition $Tk = 1.76$ (Tk is Christov's characteristic temperature and T is the experimental one), the T and TF components of the current have been obtained to be equal. The temperature measurements of the conductivity have been limited by the glass transition temperature

of the glasses studied [10], because of thermocrystallization processes. The activation energy of the conductivity E_a has been determined from these dependences (Fig. 5).

Table I. Effective electron mass and electron work function for thermionic and thermionic-field emissions of the studied samples.

Composition	m^*	ϕ_T	ϕ_{TF}
$\text{Ge}_{33}\text{S}_{67}$	0.51	0.81	0.81
$\text{Ge}_{32}\text{S}_{64}\text{Ga}_4$	0.55	0.82	0.81
$\text{Ge}_{31}\text{S}_{61}\text{Ga}_8$	0.68	0.81	0.80
$\text{Ge}_{29}\text{S}_{59}\text{Ga}_{12}$	0.99	0.80	0.79

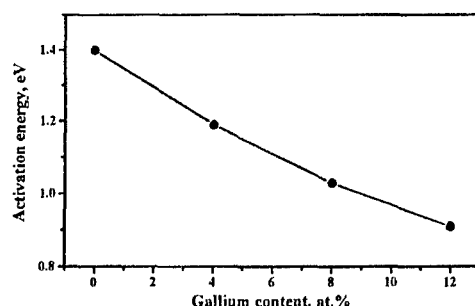


Fig. 5. Compositional dependence of the activation energy of the conductivity.

Subsequently, the band gap E_g^{el} can be calculated by the formula $\sigma = \sigma_0 \exp(-E_a/kT)$. The observed decrease of E_a with increasing Ga can be explained by the local ordering structure of the studied glasses [16]. The formation of Ga-Ga bridges at highest Ga contents leads to creation of defect states, resulting in an increase of the electron density in the conduction band.

4. Conclusion

The complex investigation of the optical and electrical properties of amorphous $(\text{GeS}_2)_{100-x}\text{Ga}_x$ thin films shows that the introduction of Ga into glassy GeS_2 does not influence significantly the glass. The results from the electrical transport in the thermionic and thermionic-field emission regions support Christov's theory for injected electron currents in insulators and semiconductors. The studied films are characterized by their basic optical (band gap, refractive index) and electrical (effective electron mass, electron work function, activation energy of the conductivity, etc.) properties.

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